

# Supporting Information for

## Impacts of environmental and engineered

## processes on the PFAS fingerprint of

## fluorotelomer-based AFFF

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## Section S1. Materials and Methods

**Purchased Chemicals.** Methanol (HPLC grade), acetonitrile (HPLC grade), potassium persulfate (ACS grade), ammonium acetate (LC-MS grade), and acetic acid (glacial) were purchased from Fisher Chemical. Sodium phosphate dibasic (ACS reagent  $\geq 99\%$ ) was purchased from Sigma-Aldrich. Sodium phosphate monobasic anhydrous (reagent grade) was purchased from Amresco. Ammonium hydroxide (30% reagent grade) was purchased from VWR-Baker. Ammonium acetate (ACS reagent  $\geq 98\%$ ) was purchased from Honeywell-Fluka. Washed Ottawa Sand was purchased from EMD Chemicals. All PFAS standards were purchased from Wellington Laboratories (**Table S1**). Ultrapure water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ) was supplied by a Milli-Q water system.

**Table S1.** PFAS analytes, surrogates, and internal standards used in this study.

Compound Type	Product Code or CAS Number	Compound(s)
Analytes	PFAC-MXB	Perfluoro-n-butanoic acid (PFBA)
		Perfluoro-n-pentanoic acid (PFPeA)
		Perfluoro-n-hexanoic acid (PFHxA)
		Perfluoro-n-heptanoic acid (PFHpA)
		Perfluoro-n-octanoic acid (PFOA)
		Perfluoro-n-nonanoic acid (PFNA)
		Perfluoro-n-decanoic acid (PFDA)
		Perfluoro-n-undecanoic acid (PFUdA)
		Perfluoro-n-dodecanoic acid (PFDoA)
		Perfluoro-n-tridecanoic acid (PFTrDA)
		Perfluoro-n-tetradecanoic acid (PFTeDA)
		Perfluoro-n-hexadecanoic acid (PFHxDA)
		Perfluoro-n-octadecanoic acid (PFODA)
		Potassium perfluoro-1-butanefluorobutanesulfonate (PFBS)
		Sodium perfluoro-1-hexanesulfonate (PFHxS)
		Sodium perfluoro-1-octanesulfonate (PFOS)
		Sodium perfluoro-1-decanesulfonate (PFDS)
Surrogates	L-PFHpS	Sodium perfluoro-1-heptanesulfonate (PFHpS)
	4:2 FTS	Sodium 1H,1H, 2H, 2H-perfluorohexane sulfonate
	6:2 FTS	Sodium 1H,1H, 2H, 2H-perfluorooctane sulfonate
	8:2 FTS	Sodium 1H,1H, 2H, 2H-perfluorodecane sulfonate
	10:2 FTS	Sodium 1H,1H, 2H, 2H-perfluorododecane sulfonate
	MPFAC-MXA	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid (M4PFBA)
		Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid (M2PFHxA)
		Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid (M4PFOA)
		Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid (M5PFNA)
		Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid (M2PFDA)
		Sodium perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate (M2PFHxS)
		Sodium perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ] octanesulfonate (M4PFOS)
	M3PFBS	(Na) Perfluoro-1-[234- <sup>13</sup> C <sub>3</sub> ]butanesulfonate
	M2-4:2FTS	(Na) 1H,1H,2H,2H-perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]hexane sulfonate
	M2-6:2FTS	(Na) 1H,1H,2H,2H-perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]octane sulfonate
	M2-8:2FTS	(Na) 1H,1H,2H,2H-perfluoro[1,2- <sup>13</sup> C <sub>2</sub> ]decane sulfonate
Internal Standards	M2PFOA	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]octanoic acid
	M8PFOS	(Na) Perfluoro[ <sup>13</sup> C <sub>8</sub> ]octanoic acid
Precursors	1432486-88-8	4:2 Fluorotelomer thioether amido sulfonate (4:2 FtTAoS)
	88992-47-6	6:2 Fluorotelomer thioether amido sulfonate (6:2 FtTAoS)
	1383439-45-9	8:2 Fluorotelomer thioether amido sulfonate (8:2 FtTAoS)
	88992-46-5	6:2 Fluorotelomer thiohydroxy ammonium (6:2 FtTHN <sup>+</sup> )

**Table S2.** Collection date and coordinates for each of the locations sampled.

Site Name	Date Collected	Coordinates	
		N	W
GB Shore Control	July 1, 2021	45.086995	87.587409
GB Shore 1	July 2, 2021	45.07894	87.60674
GB Shore 2	July 2, 2021	45.07343	87.6112
GB Shore 3	July 2, 2021	45.071341	87.61256
GB Shore 4	July 2, 2021	45.06712	87.61466
GB Shore 5	July 2, 2021	45.06155	87.61805
GB Shore 6	July 2, 2021	45.05578	87.62137
Peshtigo River 1	June 30, 2021	45.21387	87.954385
Peshtigo River 2	June 30, 2021	45.046692	87.744237
Peshtigo River 3	June 30, 2021	44.989011	87.66582
Menominee River 1	July 1, 2021	45.195358	87.742428
Menominee River 2	July 1, 2021	45.111968	87.658653
Menominee River 3	July 1, 2021	45.102669	87.62902
Little River 1	July 1, 2021	45.042166	87.656017
Little River 2	July 2, 2021	45.04492	87.62631
Ditch A	July 1, 2021	45.063448	87.637883
Ditch B Upstream	July 1, 2021	45.076277	87.621489
Ditch B Downstream	July 2, 2021	45.072536	87.612717
Gravelly Brook 1	July 1, 2021	45.179039	87.847205
Gravelly Brook 2	July 1, 2021	45.164728	87.857505
Gravelly Brook 3	June 30, 2021	45.158827	87.904572
Gravelly Brook 4	July 1, 2021	45.15028	87.876293
Beaver Creek	June 30, 2021	45.12823	87.987144
Unnamed Creek	June 30, 2021	45.083781	87.76832
Mudbrook Creek 1	July 1, 2021	45.179168	87.805762
Mudbrook Creek 2	July 1, 2021	45.164446	87.821074
Mudbrook Creek 3	June 30, 2021	45.149942	87.821222

**Aqueous Extraction Method.** Briefly, 250 mL samples were buffered using 1 g/L ammonium acetate and mass-labeled surrogate standards were added. PFAS were extracted by solid-phase extraction (SPE) onto weak anion exchange cartridges (Phenomenex Strata X-AW) and eluted with 2% ammonium hydroxide in methanol. Extracts were dried under a gentle stream of nitrogen, amended with mass-labeled internal standards, and diluted to 1.0 mL with methanol:Milli-Q water (80:20, v:v).

**Sediment Extraction Method.** Prior to extraction, sediments were dried at room temperature, homogenized using an agate mortar and pestle, and sieved through No. 100 mesh. 2g of dry sediment was weighed into a 15 mL falcon tube and mass-labeled surrogate standards were added. A 10 mL extraction solution of methanol:Milli-Q water (80:20, v:v) was added and samples were placed on a shaker table for one hour. Samples were adjusted to pH 9-10 using ammonium hydroxide, centrifuged, and filtered (0.2  $\mu$ m nylon). The filtered supernatant was adjusted to pH 3-4 using acetic acid and analyzed by LC-MS/MS.

**LC-MS/MS Method.** PFAS concentrations were quantified on an Agilent 1260 LC system equipped with an Agilent 6460 triple quadrupole mass spectrometer. PFAS were quantified using an optimized method based on previously documented methods.<sup>1,2</sup> Where possible, linear and branched isomers were resolved by variation in retention time. This was possible for PFHxA, PFHxS, PFHpA, PFHpS, PFOA, PFOS, PFNA, PFDA, and PFUdA. Parameters for precursors were determined in a previous study.<sup>3</sup> No standards were used for these compounds. All compounds were detected using negative electrospray ionization except for 6:2 FtTHN<sup>+</sup>, which was detected in positive mode in the same LC-MS/MS run.

Analytical column:	Agilent ZORBAX Eclipse Plus C18	
Delay column:	Agilent Eclipse Plus C18	
Injection volume:	5 $\mu$ L	
Flow Rate:	0.6 mL/min	
Mobile phase:	A: 20 mM Ammonium Acetate (filtered through a 0.2 $\mu$ m nylon filter)	
	B: 100% Methanol	
Column temperature:	50°C	
Gradient:	Time (min)	%B
	0.0	10
	0.5	10
	2.0	30
	14.0	95
	14.5	100

Retention Time (min):	Compound	Linear	Branched
	PFBA	5.25	
	PFPeA	7.79	
	PFBS	8.18	
	4:2 FtTAoS	8.60	
	4:2 FTS	9.40	
	PFHxA	9.53	9.27
	PFHpA	10.78	10.55
	PFHxS	10.84	10.61
	6:2 FtTAoS	11.48	
	6:2 FTS	11.72	
	PFOA	11.76	11.55
	PFHpS	11.77	11.53
	PFOS	12.53	12.29; 12.06
	PFNA	12.55	12.34
	PFDA	13.21	13.04
	8:2 FTS	13.21	
	PFDS	13.73	
	PFUdA	13.77	13.62
	8:2 FtTAoS	14.14	
	PFDaA	14.25	
	10:2 FTS	14.28	
	PFTTrDA	14.65	
	PFTeDA	15.00	
	6:2 FtTHN <sup>+</sup>	15.43	
	PFHxDA	15.55	
	PFODA	15.96	

Stop time: 18.5 min

Post time: 4 min

**Table S3.** Previously determined acquisition parameters for precursors compounds.<sup>3</sup>

Analyte	Precursor Ion ( <i>m/z</i> )	Product Ion ( <i>m/z</i> )	Fragmentor (V)	Collision Energy (V)
4:2 FtTAoS	486	135	62	38
		80		56
6:2 FtTAoS	586	135	64	40
		80		64
8:2 FtTAoS	686	135	78	44
		80		68
6:2 FtTHN <sup>+</sup>	496	79	54	44
		393		34

**PCA Calculations.** Samples were grouped by principal component analysis (PCA) using the normalized distribution of the 22 targeted PFAS in each sample. PCA was conducted in R using the `prcomp` function. PCA was performed for all aqueous samples, all sediment samples, and all aqueous and sediment samples combined.

## **Section S2. Quality Control**

**Field Sampling.** Equipment was chosen to avoid PFAS-containing materials, such as Teflon. Nitrile gloves were worn at all times and only PFAS-free clothing and materials were used. In the field, one field reagent blank was performed each day of sampling. A 250 mL polypropylene bottle of Milli-Q water was taken to the field site, poured into a separate 250 mL polypropylene bottle, and treated the same as other samples to ensure no PFAS contamination was introduced during sampling and handling. Upon analysis, no method analytes were detected in any of the field reagent blanks.

**Laboratory Analysis.** An initial demonstration of capability was performed for water analysis as described by EPA 533.<sup>2</sup> This included demonstrating low LC system background, calibration verification using a quality control standard (a calibration standard purchased and prepared separately from calibration solutions, must be 70 – 130% of the true value), precision of solid-phase extraction (SPE; %RSD <20% for seven replicates), accuracy of solid-phase extraction (average recovery within 70 – 130% for each analyte in seven replicates), and determination of minimum reporting levels (mean concentration plus three times the standard deviation of a series of blanks). Ongoing quality control included analysis of a laboratory reagent blank (Milli-Q water, extracted by SPE), laboratory fortified blank (Milli-Q water spiked with analytes, extracted by SPE), laboratory fortified sample matrix (site sample, spiked with analytes, extracted with SPE),

and field duplicate, each performed for every group of 20 samples. All laboratory-fortified samples were between 70 – 130% of the true value. Calibration checks were performed every 10 samples. In all water samples, isotope dilution was performed by adding spikes of surrogates before SPE and adding internal standards after SPE.

For sediment extraction, an initial demonstration of performance was performed as described by ASTM D7968.<sup>4</sup> This included analyzing four replicates of spiked Ottawa sand containing analytes and surrogates. Each sample was taken through full extraction and analyzed via LC-MS/MS (%RSD <30%). Ongoing quality control included analysis of a method blank (Ottawa sand), reporting limit check sample (Ottawa sand spiked with 1 – 2 times the reporting limit), laboratory control sample (Ottawa sand spiked with mid-level concentration), matrix spike (site sample spiked with analytes), and matrix spike duplicate, each performed every group of 20 samples. In all sediment samples, isotope dilution was performed by adding surrogate spikes before extraction.

**Table S4.** Average recoveries of mass-labeled surrogates and internal standards in all extracted surface water samples (n = 27) and TOP surface water samples (n = 27). TOP surface water extracts did not have internal standards added. According to EPA Method 533,<sup>2</sup> the recovery for surrogate compounds must be between 50-200% and the recovery for internal standards must be between 30-170%.

	<b>Surface Water</b>		<b>TOP Surface Water</b>	
<b>Surrogate Compound</b>	<b>Average Recovery (%)</b>	<b>Standard Deviation</b>	<b>Average Recovery (%)</b>	<b>Standard Deviation</b>
M4PFBA	59	15	66	19
M3PFBS	90	11	100	17
M2PFHxA	80	9	81	15
M2-4:2 FTS	154	20	88	19
M4PFHxS	86	9	97	18
M4PFOA	76	8	80	16
M2-6:2 FTS	127	33	96	22
M5PFNA	80	7	83	18
M4PFOS	78	6	100	20
M2PFDA	77	8	82	18
M2-8:2 FTS	145	22	103	24
<b>Internal Standard</b>	<b>Average Recovery (%)</b>	<b>Standard Deviation</b>	<b>Average Recovery (%)</b>	<b>Standard Deviation</b>
M2PFOA	105	10	NA	NA
M8PFOS	102	10	NA	NA

**Table S5.** Average recoveries of mass-labeled surrogates in all extracted field sediment samples (n = 24).

<b>Surrogate Compound</b>	<b>Average Recovery (%)</b>	<b>Standard Deviation</b>
M4PFBA	110	3
M3PFBS	109	5
M2PFHxA	105	3
M2-4:2 FTS	88	10
M4PFHxS	100	7
M4PFOA	104	5
M2-6:2 FTS	93	9
M5PFNA	99	7
M4PFOS	102	12
M2PFDA	103	7
M2-8:2 FTS	90	23

**Table S6.** Minimum reporting limits (MRLs) of analytes after extraction. Results below these concentrations are reported as below detection (BD). Surrogates for each native analyte are used for recovery screening and correction.

	<b>Sediment MRL (ng/kg)</b>	<b>Aqueous MRL (ng/L)</b>	<b>Surrogate</b>
PFBA	123	0.4	M4PFBA
PFPeA	30	0.4	M2PFHxA
PFBS	11	0.4	M3PFBS
PFHxA	23	0.4	M2PFHxA
4:2 FTS	5	0.4	M2-4:2 FTS
PFHpA	42	0.4	M2PFHxA
PFHxS	9	0.4	M4PFHxS
PFOA	5	0.4	M4PFOA
6:2 FTS	3	0.4	M2-6:2 FTS
PFHpS	8	0.4	M4PFHxS
PFNA	45	0.4	M5PFNA
PFOS	45	0.4	M4PFOS
PFDA	32	0.4	M2PFDA
8:2 FTS	26	0.4	M2-8:2 FTS
PFUdA	27	0.4	M2PFDA
PFDS	8	0.4	M4PFOS
PFDoA	48	0.4	M2PFDA
10:2 FTS	27	0.4	M2-8:2 FTS
PFTTrDA	35	0.4	M2PFDA
PFTeDA	106	0.4	M2PFDA
PFHxDA	35	0.4	M2PFDA
PFODA	30	0.4	M2PFDA

**Table S7.** Results from laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), and field reagent blanks (FRB) after aqueous sample extraction and analysis. Laboratory fortified samples were spiked with 20 ng/L of each PFAS in 250 mL; percent recoveries are noted in parentheses. Samples noted with BD were below the minimum reporting limit shown in **Table S6**.

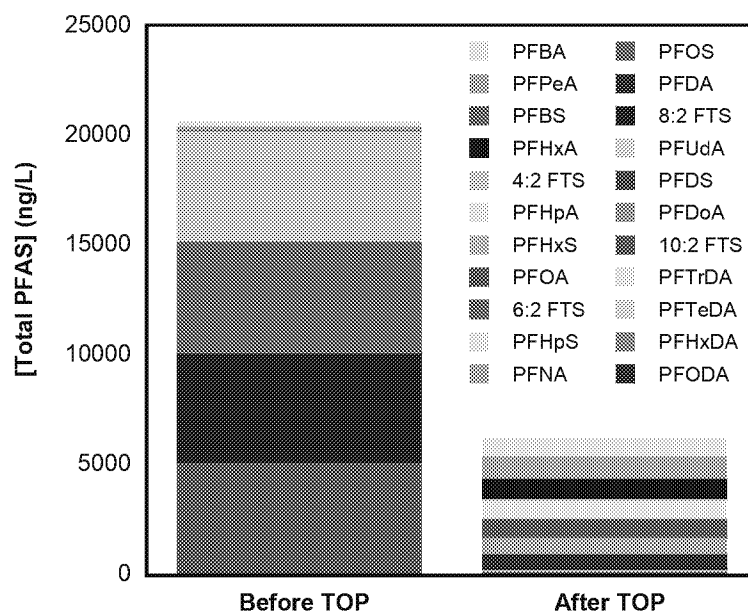
	Aqueous Concentration (ng/L)					
	LRB 1	LRB 2	LFB 1	LFB 2	FRB 1	FRB 2
PFBA	BD	BD	17 (85%)	17 (85%)	BD	BD
PFPeA	BD	BD	17 (85%)	16 (80%)	BD	BD
PFBS	BD	BD	17 (85%)	18 (90%)	BD	BD
PFHxA	BD	BD	18 (90%)	16 (80%)	BD	BD
4:2 FTS	BD	BD	17 (85%)	16 (80%)	BD	BD
PFHpA	BD	BD	17 (85%)	17 (85%)	BD	BD
PFHxS	BD	BD	17 (85%)	16 (80%)	BD	BD
PFOA	BD	BD	17 (85%)	16 (80%)	BD	BD
6:2 FTS	BD	BD	19 (95%)	16 (80%)	BD	BD
PFHpS	BD	BD	18 (90%)	17 (85%)	BD	BD
PFNA	BD	BD	18 (90%)	17 (85%)	BD	BD
PFOS	BD	BD	17 (85%)	17 (85%)	BD	BD
PFDA	BD	BD	18 (90%)	17 (85%)	BD	BD
8:2 FTS	BD	BD	17 (85%)	18 (90%)	BD	BD
PFUdA	BD	BD	19 (95%)	17 (85%)	BD	BD
PFDS	BD	BD	18 (90%)	17 (85%)	BD	BD
PFDoA	BD	BD	19 (95%)	16 (80%)	BD	BD
10:2 FTS	BD	BD	16 (80%)	17 (85%)	BD	BD
PFTTrDA	BD	BD	19 (95%)	17 (85%)	BD	BD
PFTeDA	BD	BD	19 (95%)	16 (80%)	BD	BD
PFHxDA	BD	BD	17 (85%)	17 (85%)	BD	BD
PFODA	BD	BD	17 (85%)	17 (85%)	BD	BD

**Table S8.** Results from sediment blanks, reporting limit check samples (RLCS; 100 ng/kg), lab controls (500 ng/kg), matrix spikes (MS; 500 ng/kg), and matrix spike duplicates (MSD; 500 ng/kg) after sediment sample extraction and analysis. Percent recoveries for RLCS, controls, and matrix spikes are noted in parentheses. Samples noted with BD were below the minimum reporting limit shown in **Table S6**.

	Sediment Concentration (ng/kg)						
	Blank 1	Blank 2	RLCS	Lab Control	Peshtigo River 3	Peshtigo River 3 MS	Peshtigo River 3 MSD
PFBA	BD	BD	154 (154%)	477 (95%)	BD	512 (102%)	513 (103%)
PFPeA	BD	BD	118 (118%)	412 (82%)	BD	413 (83%)	435 (87%)
PFBS	BD	BD	106 (106%)	383 (77%)	BD	374 (75%)	418 (84%)
PFHxA	BD	BD	97 (97%)	400 (80%)	BD	406 (81%)	437 (87%)
4:2 FTS	BD	BD	100 (100%)	358 (72%)	BD	381 (76%)	357 (71%)
PFHpA	BD	BD	113 (113%)	413 (83%)	BD	449 (90%)	426 (85%)
PFHxS	BD	BD	92 (92%)	346 (69%)	BD	402 (80%)	418 (84%)
PFOA	BD	BD	105 (105%)	411 (82%)	11	414 (83%)	442 (88%)
6:2 FTS	BD	BD	64 (64%)	393 (79%)	4	429 (86%)	409 (82%)
PFHpS	BD	BD	85 (75%)	359 (72%)	BD	369 (74%)	399 (80%)
PFNA	BD	BD	105 (105%)	426 (85%)	BD	395 (79%)	427 (85%)
PFOS	BD	BD	92 (92%)	390 (78%)	48	488 (98%)	408 (82%)
PFDA	BD	BD	96 (96%)	331 (66%)	BD	510 (102%)	375 (75%)
8:2 FTS	BD	BD	80 (80%)	393 (79%)	BD	425 (85%)	376 (75%)
PFUdA	BD	BD	95 (95%)	400 (80%)	BD	396 (79%)	392 (78%)
PFDS	BD	BD	125 (125%)	442 (88%)	BD	458 (92%)	398 (80%)
PFDdA	BD	BD	99 (99%)	374 (75%)	BD	324 (65%)	387 (77%)
10:2 FTS	BD	BD	60 (60%)	365 (73%)	BD	418 (84%)	381 (76%)
PFTTrDA	BD	BD	93 (93%)	383 (77%)	BD	449 (90%)	400 (80%)
PFTeDA	BD	BD	131 (131%)	414 (83%)	BD	475 (95%)	500 (100%)
PFHxDA	BD	BD	112 (112%)	370 (74%)	BD	357 (71%)	385 (77%)
PFODA	BD	BD	77 (77%)	341 (68%)	BD	438 (88%)	473 (95%)

**Table S9.** Results from TOP assay method checks on a Milli-Q sample spiked with FTS compounds. The 250 mL sample was spiked with 20 ng/L each FTS compounds, underwent TOP assay, and then was concentrated by 250 during SPE before being analyzed by LC-MS/MS. CF<sub>2</sub> groups were calculated for oxidized FTS by ([Before TOP] – [After TOP]) x CF<sub>2</sub> groups in a single compound. CF<sub>2</sub> groups were calculated for PFCAs formed by ([After TOP] – [Before TOP]) x CF<sub>2</sub> groups in a single compound.

	Concentration (ng/L)		CF <sub>2</sub> Groups	
	Before TOP	After TOP	From Oxidized FTS	To PFCAs Formed
PFBA	249	807		1672
PFPeA	168	1007		3355
PFBS	22	22		
PFHxA	16	924		4538
4:2 FTS	5003	48	19818	
PFHpA	10	833		4938
PFHxS	20	23		
PFOA	32	788		5298
6:2 FTS	5036	99	29621	
PFHpS	2	2		
PFNA	0	711		5690
PFOS	7	10		
PFDA	9	670		5946
8:2 FTS	5007	57	39601	
PFUdA	30	72		422
PFDS	0	1		
PFDoA	6	10		42
10:2 FTS	5002	98	49044	
PFTTrDA	7	6		
PFTeDA	11	4		
PFHxDA	26	24		
PFODA	36	22		
		<b>Total</b>	138084	31901
		<b>% CF<sub>2</sub> Converted</b>	<b>23</b>	



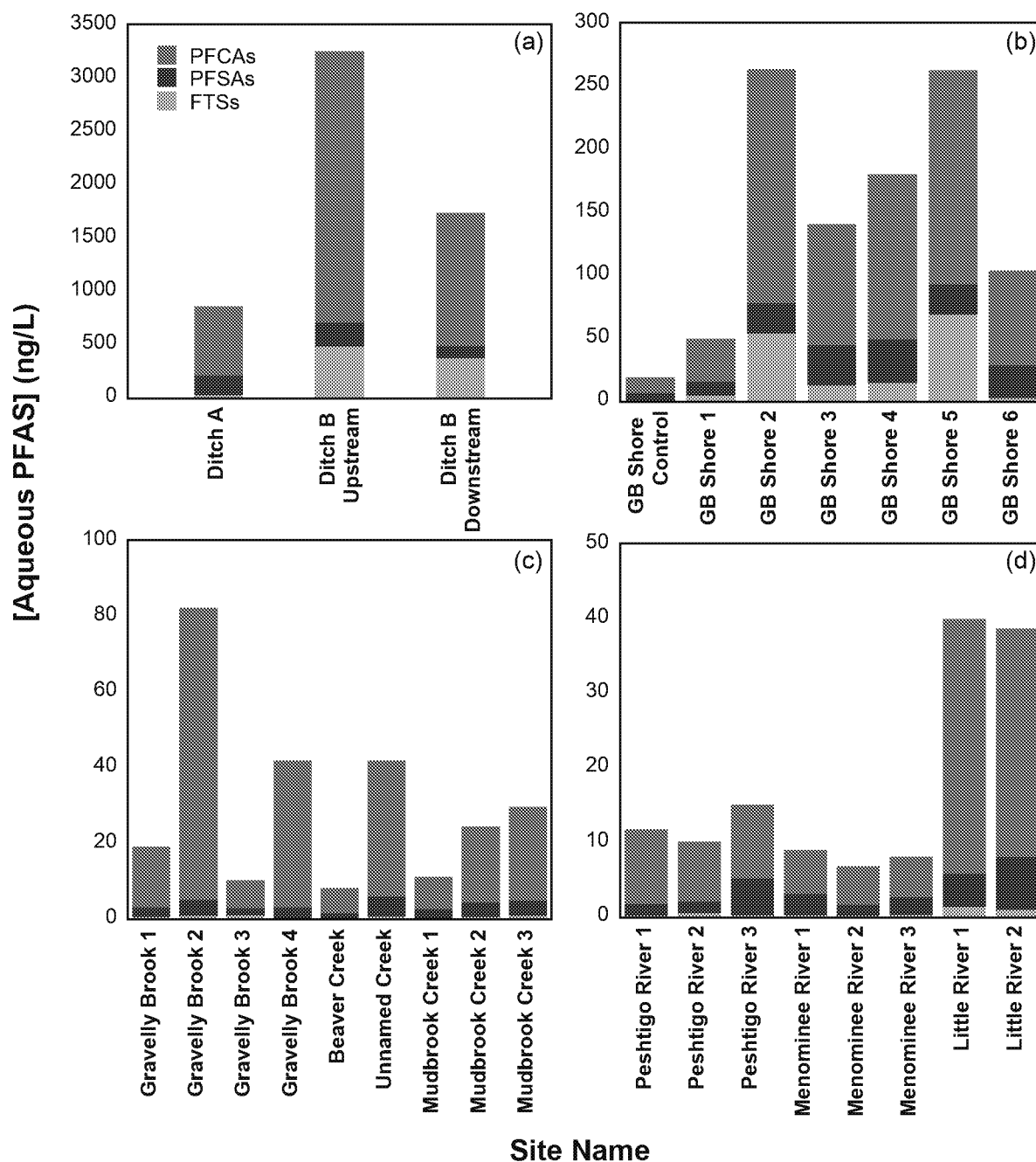
**Figure S1.** Concentrations of each PFAS before and after TOP on a Milli-Q sample spiked with FTS compounds. Compounds are ordered by retention time.

### Section S3. Site Water Characterization

**Table S10.** Total suspended solids (TSS) in site waters as determined by filtering 250 mL of site water on a pre-weighed 1 µm polycarbonate filter. BD indicates that TSS was below detection. Site water pH was measured within 5 days of collection.

Site Name	TSS (mg/L)	pH
GB Shore Control	63.96	7.64
GB Shore 1	71.96	8.15
GB Shore 2	37.53	8
GB Shore 3	50.61	8.02
GB Shore 4	37.40	8.01
GB Shore 5	BD	7.96
GB Shore 6	284.73	7.87
Peshtigo River 1	BD	7.81
Peshtigo River 2	BD	8.06
Peshtigo River 3	BD	8.24
Menominee River 1	46.81	7.68
Menominee River 2	BD	7.58
Menominee River 3	BD	7.68
Little River 1	17.89	7.74
Little River 2	BD	7.66
Ditch A	BD	7.15
Ditch B Upstream	BD	7.4
Ditch B Downstream	BD	7.39
Gravelly Brook 1	BD	7.58
Gravelly Brook 2	0.50	7.67
Gravelly Brook 3	BD	7.61
Gravelly Brook 4	4.01	7.77
Beaver Creek	29.51	7.27
Unnamed Creek	BD	7.62
Mudbrook Creek 1	BD	7.47
Mudbrook Creek 2	BD	7.71
Mudbrook Creek 3	6.73	7.9

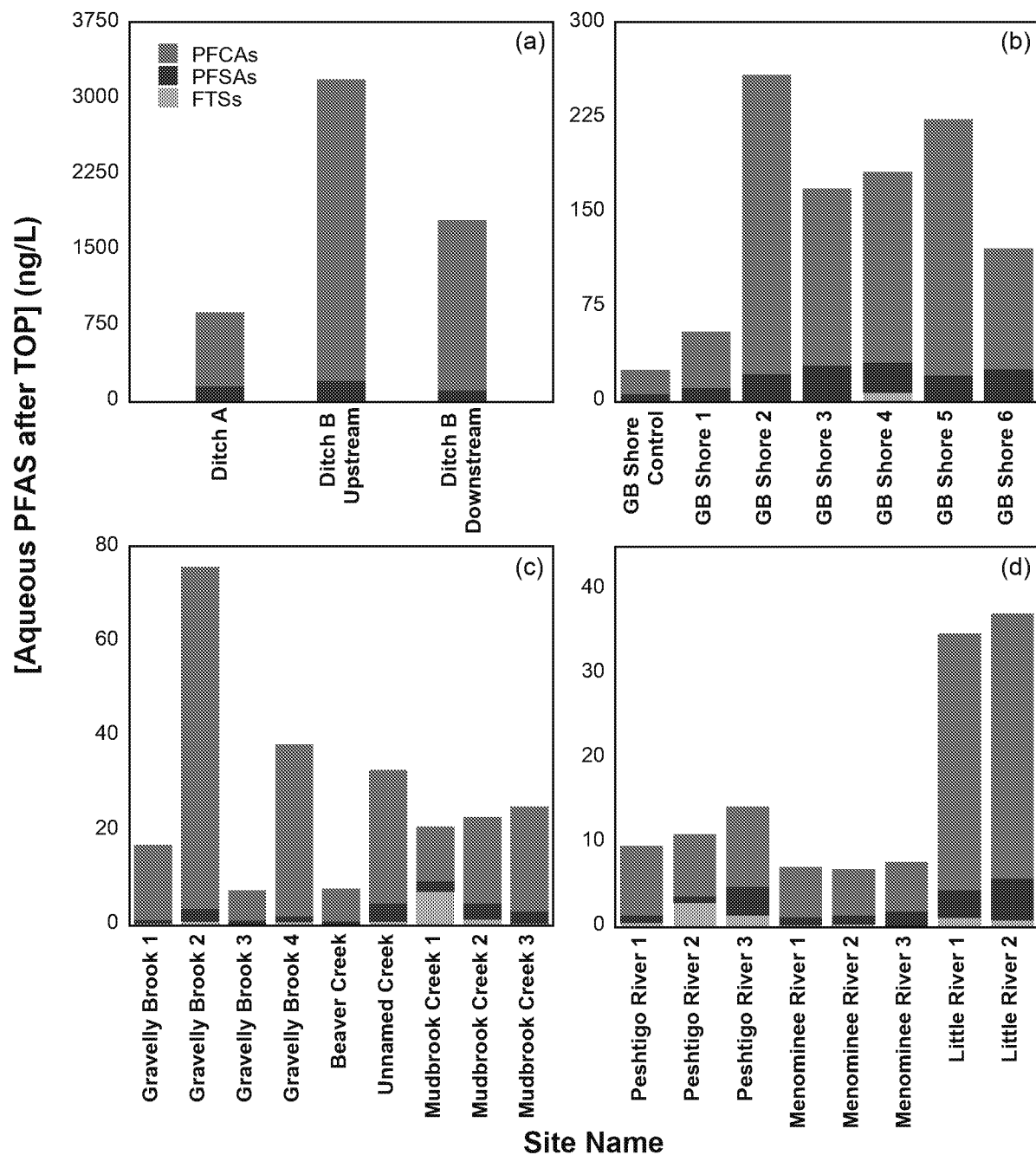
## Section S4. PFAS Quantification



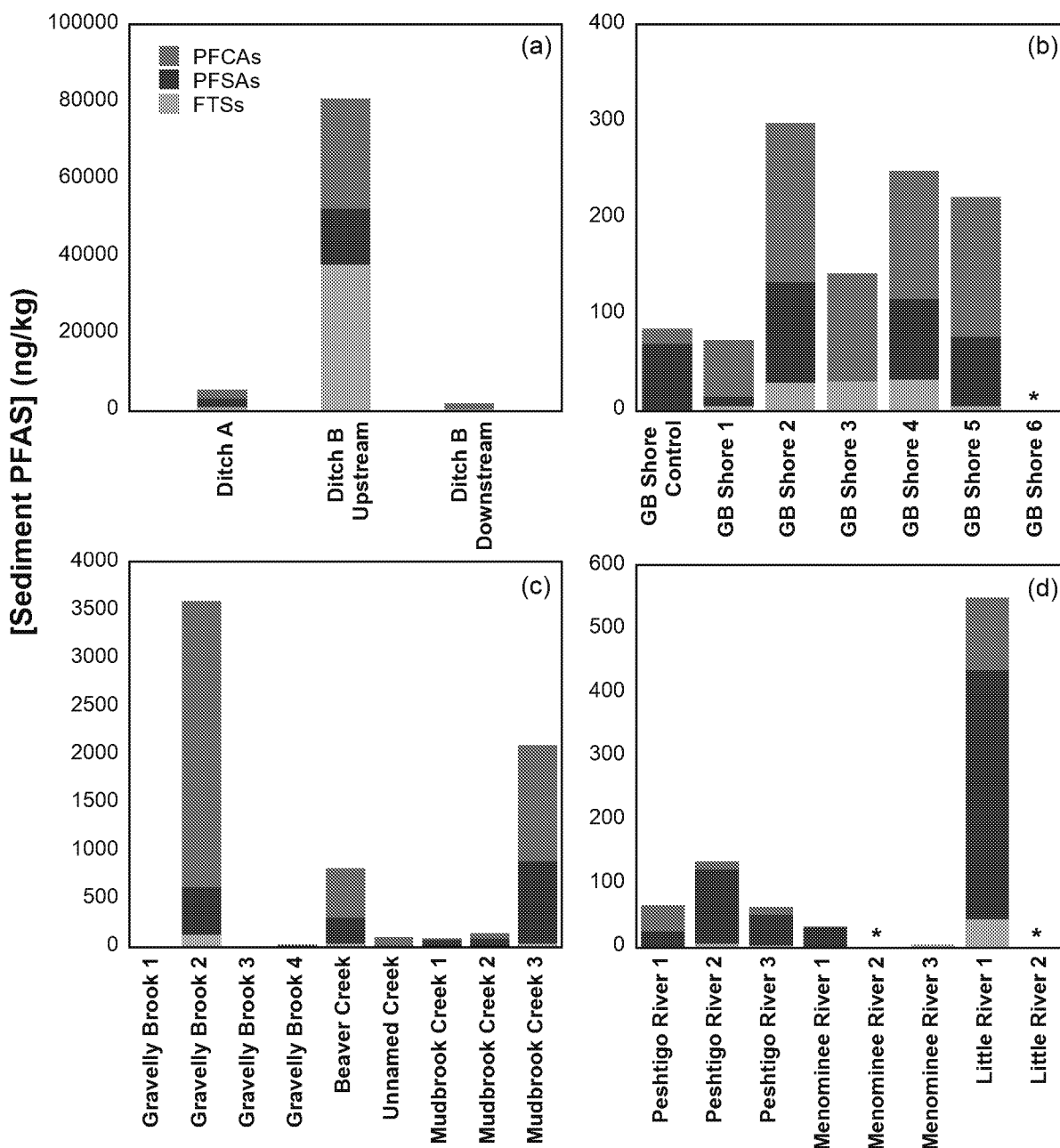
**Figure S2.** PFAS concentrations in site water at (a) drainage ditches, (b) Green Bay (GB) shoreline, (c) biosolids fields tributaries, and (d) rivers. PFAS concentrations are grouped as perfluorinated carboxylic acids (PFCAs), perfluorinated sulfonic acids (PFSA), and fluorotelomer sulfonates (FTSs). Tabulated data for 22 individual PFAS is available in **Table S11**.

**Table S12.** Results from precursor analysis on site waters. All peak areas have been filtered by retention time and adjusted to reflect peak areas for 1 L initial volume.

Site Name	Peak Area (a.u.)			
	4:2 FtTAoS	6:2 FtTHN <sup>+</sup>	6:2 FtTAoS	8:2 FtTAoS
GB Shore Control	3.85	954.57	9.79	6.15
GB Shore 1	16.14	1306.31	81.98	6.75
GB Shore 2		4743.31	557.30	6.93
GB Shore 3		648.09	470.59	6.72
GB Shore 4		1043.47	31.56	2.14
GB Shore 5	8.04		152.77	7.67
GB Shore 6		1774.85	490.72	7.25
Peshtigo River 1			40.29	2.83
Peshtigo River 2	3.46		296.70	3.96
Peshtigo River 3		19.57	606.51	12.36
Menominee River 1			85.20	5.86
Menominee River 2	6.97		23.84	10.06
Menominee River 3	3.13		44.29	5.13
Little River 1			42.62	17.37
Little River 2	12.87	173.09	35.59	6.60
Ditch A		30.50	218.74	1.58
Ditch B Upstream			572.43	7.67
Ditch B Downstream		93.85	7.92	0.00
Gravelly Brook 1	10.12		34.06	17.72
Gravelly Brook 2			33.69	4.85
Gravelly Brook 3	3.65	59.12	182.78	7.11
Gravelly Brook 4	11.55		67.59	
Beaver Creek	7.48		22.78	9.27
Unnamed Creek	7.47			4.28
Mudbrook Creek 1	4.95		445.81	12.10
Mudbrook Creek 2	5.78	254.41	6.86	8.21
Mudbrook Creek 3			87.79	1.61



**Figure S3.** PFAS concentrations in site water after oxidation via TOP assay from (a) drainage ditches, (b) Green Bay (GB) shoreline, (c) biosolids fields tributaries, and (d) rivers. PFAS concentrations are grouped in perfluorinated carboxylic acids (PFCAs), perfluorinated sulfonic acids (PFSAs), and fluorotelomer sulfonates (FTSs). Tabulated data for 22 individual PFAS is available in **Table S13**.



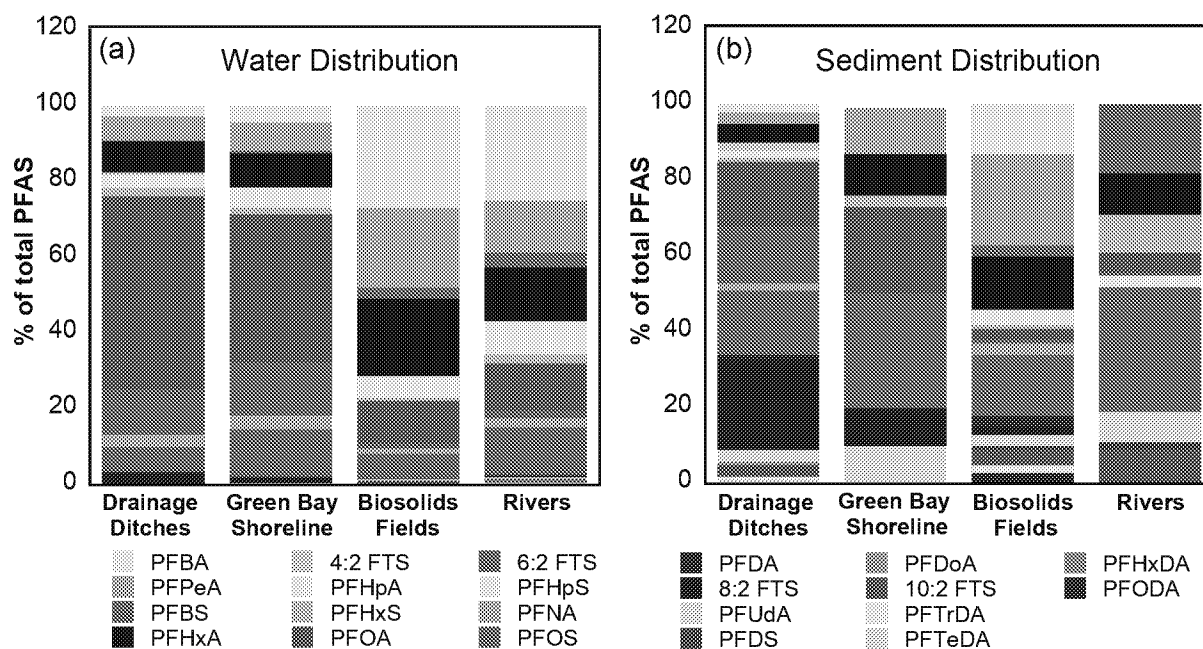
**Figure S4.** PFAS concentrations in site sediment at (a) drainage ditches, (b) Green Bay (GB) shoreline, (c) biosolids fields tributaries, and (d) rivers. PFAS concentrations are grouped as perfluorinated carboxylic acids (PFCAs), perfluorinated sulfonic acids (PFSA), and fluorotelomer sulfonates (FTS). Tabulated data for 22 individual PFAS is available in **Table S14**.

**Table S15.** Average partition coefficients calculated using field measurements. Compounds are organized by number of fluorinated carbons and functional groups. Numbers of sites used in each calculation are listed in parentheses. Only sites with measureable concentrations in both water and sediment were used to calculate partition coefficients.

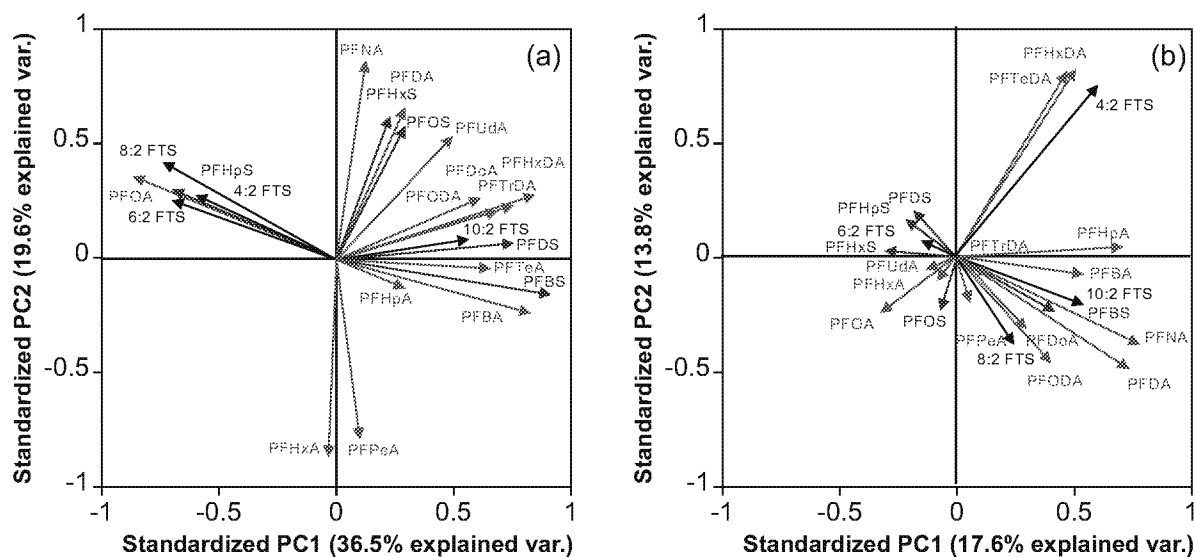
# of Carbons	Average log $K_d$ (L/kg)		
	PFCA	PFSA	FTS
3	1.24 ± 0.30 (4)		
4	1.52 ± 0.76 (10)	1.69 ± 0.27 (5)	2.74 ± 0.58 (2)
5	1.44 ± 0.95 (12)		
6	1.21 ± 0.48 (5)	1.71 ± 0.50 (12)	1.10 ± 0.46 (11)
7	1.20 ± 0.96 (19)	1.32 (1)	
8	2.07 ± 0.53 (6)	1.92 ± 0.56 (15)	2.91 ± 0.98 (6)
9	2.74 ± 0.53 (5)		
10	2.98 ± 0.55 (8)	3.67 ± 1.00 (6)	2.85 ± 0.64 (6)
11	3.45 ± 0.39 (2)		
12	3.56 ± 0.36 (3)		
13	3.76 (1)		
15	3.01 (1)		
17	3.31 ± 0.09 (2)		

**Table S16.** Results from precursor analysis on site sediments. All peak areas have been filtered by retention time and adjusted to reflect peak areas for 1 kg initial mass.

Site Name	Peak Area (a.u.)			
	4:2 FtTAoS	6:2 FtTHN <sup>+</sup>	6:2 FtTAoS	8:2 FtTAoS
GB Shore Control			1.41	5.87
GB Shore 1				
GB Shore 2	15.63			11.63
GB Shore 3	1.84			
GB Shore 4				
GB Shore 5	1.87		10.17	21.41
Peshtigo River 1	2.28		3.10	
Peshtigo River 2	1.15			
Peshtigo River 3				
Menominee River 1			4.83	33.90
Menominee River 3	2.25		19.10	10.68
Little River 1	2.73		6.95	31.29
Ditch A		32.04		13.29
Ditch B Upstream	9.88		7.87	
Ditch B Downstream				
Gravelly Brook 1				14.60
Gravelly Brook 2			4.26	28.91
Gravelly Brook 3			7.58	34.12
Gravelly Brook 4			16.62	
Beaver Creek	4.81	222.31	5.09	86.84
Unnamed Creek			5.06	
Mudbrook Creek 1	9.71		3.99	25.47
Mudbrook Creek 2	3.98			
Mudbrook Creek 3	7.67		15.66	



**Figure S5.** Average PFAS distributions in (a) water and (b) sediment at each site type. Compounds are ordered by retention time.



**Figure S6.** Variables responsible for the site distributions shown in **Figure 5** in the manuscript as determined using principal component analysis on the PFAS distribution in (a) water and (b) sediment samples. Variables are color coded by compound class, with PFCAs depicted in blue, PFSA depicted in red, and FTSs depicted in black.

## Section S5. External Data

**Table S17.** PFAS concentrations<sup>5</sup> in biosolids from Marinette wastewater treatment plant, which were spread onto the agricultural fields sampled in this study.

Compound	Concentration (ug/kg)
PFHxA	290
PFHpA	3.7
PFOA	10
PFNA	3.2
PFDA	5.3
PFUdA	14
PFDoA	7.6
PFTTrDA	4.4
PFTeDA	3
PFBS	BD
PFHxS	30
PFOS	210

## References

- (1) Hunt, K.; Hindle, R.; Anumol, T. Analysis of per/polyfluoroalkyl substances in water using an Agilent 6470 Triple Quadrupole LC/MS, *Agilent Technologies*, 5991-7951EN, 2017.
- (2) Rosenblum, L.; Wendelken, S. US EPA Method 533: Determination of per-and polyfluoroalkyl substances in drinking water by isotope dilution anion exchange solid phase extraction and liquid chromatography/tandem mass spectrometry, *US EPA*, 2020.
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